

ARTICLES

Correct microcanonical ensemble in molecular dynamics

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The statistical-mechanics ensemble corresponding to equilibrium molecular dynamics simulations is different than the usual microcanonical *EVN* ensemble. Historically molecular dynamics has been associated with the *EVNM* ensemble, where \mathbf{M} is the constant total linear momentum of the system. We show that the correct ensemble associated with molecular dynamics is the *EVNMG* ensemble where \mathbf{G} is the constant of the motion associated with Galilean boosts. The ensemble associated with molecular dynamics simulations has, apparently, not been previously recognized. An earlier problem with the pressure in the new ensemble disappears. [S1063-651X(99)00305-0]

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I. INTRODUCTION

The usual microcanonical ensemble of equilibrium statistical mechanics corresponds to a system of a fixed number of particles N , in a volume V , having an energy E . In the terminology of statistical mechanics this is the *EVN* ensemble, and corresponds experimentally to an isolated system. The fact that trajectories in equilibrium molecular dynamics simulations generate an ensemble that is different than the *EVN* ensemble has long been recognized [1–3]. Because the forces are all internal forces, which obey Newton's third law, and the imposition of periodic boundary conditions removes the external force that the container walls would exert on the system of particles, the total momentum of the N particles is also conserved. The phase space must, therefore, be restricted to correspond to constant energy E and constant total linear momentum \mathbf{M} . Because we assume that the simulation uses periodic boundary conditions, the total angular momentum is not a constant of the motion and therefore plays no role in our discussions. Hence, molecular dynamics appears to generate the *EVNM* ensemble, which was named the molecular dynamics ensemble by Wood [2]. In the *EVNM* ensemble all states (\mathbf{r}, \mathbf{p}) in phase space, consistent with the given values of E , V , N , and \mathbf{M} , have equal *a priori* probability.

A comprehensive treatment of this molecular dynamics, *EVNM*, ensemble was given by Çağın and Ray [4]. They also extended the treatment to the canonical or *TVNM* ensemble [5]. In molecular dynamics this latter ensemble would be associated with one of the versions of the extended variable method of Nosé [6] to generate the canonical ensemble for the system. The treatment of the ensembles in Ref. [4] makes use of the exact Laplace transform method of treating energy shell ensembles presented by Pearson, Haliçioğlu, and Tiller [7]. In related work Lustig [8] used the method of Refs. [4,5,7] to discuss a system of rigid molecules in the *EVNM* ensemble while Friedman and Raineri [9] used the *EVNM* ensemble theory to study equal time velocity correlations in this ensemble.

One result in Refs. [4,5] was that the expression found for the pressure, by taking the derivative of the entropy with respect to the volume, was the same in the *EVN* and *EVNM* ensembles. This result was surprising because a direct application of the virial theorem from Newton's laws gives a different result in these two ensembles; the constraint of constant total momentum leads to a reduction of the number of degrees of freedom by 3 in the ideal gas part of the pressure in the virial derivation. In the present paper we resolve this problem by showing that the ensemble corresponding to molecular dynamics simulations is really the *EVNMG* ensemble, where \mathbf{G} is another quantity that is a constant of the motion. In this ensemble we obtain an expression for the pressure that agrees with the virial theorem derived from Newton's laws. Apparently this result has not been recognized before in discussions of molecular dynamics. For large N it would give only a small, $O(1/N)$, correction to the pressure. The constants of the motion represented by \mathbf{G} are associated with Galilean boosts (transformation between inertial reference frames that have infinitesimally different velocities) and \mathbf{G} is the generator of infinitesimal boosts like E is the generator of infinitesimal time translations and \mathbf{M} is the generator of infinitesimal spatial translations. The introduction of the constants \mathbf{G} into the *EVNM* ensemble corrects the problems with the pressure and related quantities in Refs. [4,5] while leaving other results unchanged and gives, finally, the correct ensemble for molecular dynamics, which is the *EVNMG* ensemble. The introduction of \mathbf{G} into the *TVNM* ensemble also corrects the pressure problem in the same way; the correct ensemble to associate with Nosé's canonical ensemble molecular dynamics is the *TVNMG* ensemble; with $\mathbf{M}=0$ [5]. The numerical value of \mathbf{G} is related to the initial position of the center of mass of the system.

II. JACOBI COORDINATES

The Hamiltonian for our system has the form of the kinetic energy of the N particles and the potential energy which we assume depends only on the interparticle dis-

tances; that is, no external fields are present,

$$\mathcal{H}(\mathbf{r}, \mathbf{p}) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}). \quad (1)$$

Many of the special forms that we shall introduce below are associated with the simple quadratic momentum dependence assumed in Eq. (1).

It is convenient to introduce a set of coordinates and momenta, referred to as Jacobi coordinates and momenta, for the later discussion of phase space integrals. These coordinates are defined so the first $N-1$ Jacobi coordinates are internal coordinates while the N th Jacobi coordinate is the center of mass coordinate of the system of particles. For N particles the Jacobi coordinates and momenta are defined by [10–12]

$$\mathbf{R}_\alpha = \frac{\sum_{i=1}^{\alpha} m_i \mathbf{r}_i}{\sum_{i=1}^{\alpha} m_i} - \mathbf{r}_{\alpha+1}, \quad \alpha = 1, 2, \dots, N, \quad \mathbf{r}_{N+1} = 0 \quad (2)$$

$$\mathbf{P}_\alpha = \frac{m_{\alpha+1}}{M_1^{\alpha+1}} \sum_{i=1}^{\alpha} \mathbf{p}_i - \frac{M_1^\alpha}{M_1^{\alpha+1}} \mathbf{p}_{\alpha+1}, \quad \alpha = 1, \dots, N-1, \quad (3)$$

$$\mathbf{P}_N = \sum_{i=1}^N \mathbf{p}_i$$

where

$$M_i^j = \sum_{k=i}^j m_k, \quad i \leq j, \quad i, j, k = 1, 2, \dots, N. \quad (4)$$

Note that the Jacobi coordinates give the position of the center of mass of the previous particles with respect to the next particle. The inverse of these transformations along with many other results concerning Jacobi coordinates and momenta are worked out in detail in Ref. [12]. The Jacobi coordinates are orthogonal and are a generalization of the usual coordinates for the center of mass and relative coordinates of a two particle system. The Jacobi coordinates are canonical, so the Jacobian (determinant of the transformation matrix) from the original Cartesian coordinates and momenta to the Jacobi coordinates and momenta is equal to one. Also the Jacobians for the transformation from the Cartesian coordi-

nates alone or the momenta alone are also equal to one [12]. The kinetic energy of the system in Jacobi coordinates is

$$K = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} = \sum_{\alpha=1}^{N-1} \frac{\mathbf{P}_\alpha^2}{2\mu_\alpha} + \frac{\mathbf{P}_N^2}{2\mu_N}, \quad (5)$$

where the reduced masses μ_α are defined by

$$\mu_\alpha = \frac{m_{\alpha+1} M_1^\alpha}{M_1^{\alpha+1}}, \quad \alpha = 1, 2, \dots, N-1, \quad \mu_N = M_1^N. \quad (6)$$

Equation (5) gives the kinetic energy in terms of the internal kinetic energy plus the kinetic energy of the center of mass and is a well known result in classical mechanics. The reduced masses satisfy the following product rule:

$$\prod_{\alpha=1}^{N-1} \mu_\alpha = \frac{\prod_{i=1}^{N-1} m_i}{\mu_N}, \quad (7)$$

where μ_N is the total mass of the system.

III. EVNMG ENSEMBLE

The *EVN* and *EVNM* ensembles have been discussed in some detail in Refs. [4,5,7] so we shall present only the details for the *EVNMG* ensemble. Because the total linear momentum of our N particle system is constant, we can integrate this equation and obtain three different constants of the motion which we call \mathbf{G} ,

$$\mathbf{G} = \sum_{i=1}^N \mathbf{p}_i t - \sum_{i=1}^N m_i \mathbf{r}_i. \quad (8)$$

Note that the value of \mathbf{G} is associated with the initial position of the center of mass and from the point of view of Galilean transformations it is the generator of transformations to inertial frames moving at infinitesimal velocities with respect to a given inertial frame [13]. We shall refer to the constraint that \mathbf{G} be constant as the boost constraint. The entropy of the system in the *EVNMG* ensemble is the logarithm of the phase volume

$$S(E, V, N, \mathbf{M}, \mathbf{G}) = k_B \ln \Phi(E, V, N, \mathbf{M}, \mathbf{G}), \quad (9)$$

where the phase volume has the form

$$\Phi(E, V, N, \mathbf{M}, \mathbf{G}) = \int \Theta(E - \mathcal{H}) \delta\left(\mathbf{M} - \sum_{i=1}^N \mathbf{p}_i\right) \cdot \delta\left(\mathbf{G} - t \sum_{i=1}^N \mathbf{p}_i + \sum_{i=1}^N m_i \mathbf{r}_i\right) d^{3N} r d^{3N} p / C_N, \quad (10)$$

and C_N is a constant, which for c different components has the value $C_N = A h^{3N} \prod_{a=1}^c N_a!$ and $N = \sum_{a=1}^c N_a$, with N_a being the number of particles of type a and A is a constant associated with the δ functions involving \mathbf{M} and \mathbf{G} , and makes the phase volume dimensionless. For the *EVN* ensemble the phase volume has the form of Eq. (10) but without the two δ function constraints and $A = 1$ [4,7]. For the *EVNM* ensemble the phase volume has the form of Eq. (10) without the δ function involving the boost constraint [4]. Transforming to Jacobi momenta in Eq. (10) and integrating over \mathbf{P}_N the phase volume becomes

$$\Phi = \int \Theta \left(E - \frac{\mathbf{M}^2}{2\mu_N} - \sum_{\alpha=1}^{N-1} \frac{\mathbf{P}_\alpha^2}{2\mu_\alpha} - U \right) \cdot \delta \left(\mathbf{G} - t\mathbf{M} + \sum_{i=1}^N m_i \mathbf{r}_i \right) d^{3(N-1)} P d^{3N} r / C_N. \quad (11)$$

In this form of the phase volume we can now carry out the integrals over the remaining Jacobi momenta using, for example, the Laplace transform method of Pearson, Halicioglu, and Tiller [7] to obtain

$$\Phi = \int \left(E - \frac{\mathbf{M}^2}{2\mu_N} - U \right)^{3(N-1)/2} \Theta \left(E - \frac{\mathbf{M}^2}{2\mu_N} - U \right) \cdot \delta \left(\mathbf{G} - t\mathbf{M} + \sum_{i=1}^N m_i \mathbf{r}_i \right) d^{3N} r / [C_0 \Gamma(3(N-1)/2 + 1)], \quad (12)$$

where

$$\begin{aligned} C_0 &= C_N \int \left((2\pi)^{3(N-1)/2} \prod_{\alpha=1}^{N-1} \mu_\alpha^{3/2} \right) \\ &= C_N \mu_N^{3/2} \int \left((2\pi)^{3(N-1)/2} \prod_{i=1}^N m_i^{3/2} \right). \end{aligned}$$

We now transform to Jacobi coordinates and carry out the integral over the center of mass coordinate in Eq. (12) to end up with

$$\begin{aligned} \Phi &= \int \left(E - \frac{\mathbf{M}^2}{2\mu_N} - U \right)^{3(N-1)/2} \\ &\times \Theta \left(E - \frac{\mathbf{M}^2}{2\mu_N} - U \right) d^{3(N-1)} R / [C_0 \Gamma(3(N-1)/2 + 1)]. \end{aligned} \quad (13)$$

This step has the effect of reducing the number of spatial integrations by 3 because the integral over the boost δ function does not change any other parts of the integrand; recall we assume the potential energy depends only on the relative coordinates and not the center of mass coordinate.

The density of states can be obtained by differentiating the phase volume with respect to the energy, which gives

$$\begin{aligned} \omega &= \frac{\partial \Phi}{\partial E} = \int \left(E - \frac{\mathbf{M}^2}{2\mu_N} - U \right)^{3(N-1)/2-1} \\ &\times \Theta \left(E - \frac{\mathbf{M}^2}{2\mu_N} - U \right) d^{3(N-1)} R / [C_0 \Gamma(3(N-1)/2)]. \end{aligned} \quad (14)$$

In order to find the average value of a quantity A we can integrate using the probability density in phase space, namely,

$$\begin{aligned} W_{EVNMG}(r, p) &= C \delta(E - \mathcal{H}) \delta \left(\mathbf{M} - \sum_{i=1}^N \mathbf{p}_i \right) \\ &\times \delta \left(\mathbf{G} - t \sum_{i=1}^N \mathbf{p}_i + \sum_{i=1}^N m_i \mathbf{r}_i \right), \end{aligned} \quad (15)$$

where C is the normalization constant. If the function A depends only on the internal spatial coordinates we may obtain the average value as an integral over configuration space using the probability density

$$\begin{aligned} W_{EVNMG}(\mathbf{R}) &= C \left(E - \frac{\mathbf{M}^2}{2\mu_N} - U \right)^{3(N-1)/2-1} \\ &\times \Theta \left(E - \frac{\mathbf{M}^2}{2\mu_N} - U \right), \end{aligned} \quad (16)$$

where the argument \mathbf{R} indicates that this probability density is a function of the internal Jacobi coordinates the same as the integrands in Eqs. (13) and (14). The average value can be written

$$\begin{aligned} \langle A \rangle &= \int A \left(E - \frac{\mathbf{M}^2}{2\mu_N} - U \right)^{3(N-1)/2-1} \\ &\times \Theta \left(E - \frac{\mathbf{M}^2}{2\mu_N} - U \right) d^{3(N-1)} R / [C_0 \Gamma(3(N-1)/2) \omega]. \end{aligned} \quad (17)$$

Various thermodynamic quantities can be obtained by taking derivatives of the entropy, for example, the temperature T and the pressure P . For the temperature

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{VN}, \quad (18)$$

which gives

$$\langle K \rangle = \langle E - U \rangle = \frac{3(N-1)}{2} k_B T + \frac{\mathbf{M}^2}{2\mu_N}, \quad (19)$$

the connection between the temperature and the average kinetic energy K . In the EVN ensemble the average kinetic energy has an N instead of $N-1$ in the internal kinetic energy part because the total momentum constraint is not included. The average in Eq. (19) is the ensemble average defined by Eq. (17); note that the kinetic energy is a function of just the configuration coordinates $\mathbf{r} = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ through the relation $K = E - U$. The pressure can be calculated from the volume derivative of the entropy

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_{EN}. \quad (20)$$

In order to carry out the volume derivative we may scale the coordinates in Eq. (13) so that the volume dependence is moved from the limits of integration explicitly into the integrand. If we call \mathbf{R}' the scaled coordinates with $\mathbf{R}' = \mathbf{R}/V^{1/3}$, then this substitution into Eq. (13) yields

$$\begin{aligned} \Phi = V^{N-1} \int \left(E - \frac{\mathbf{M}^2}{2\mu_N} - U \right)^{3(N-1)/2} \\ \times \Theta \left(E - \frac{\mathbf{M}^2}{2\mu_N} - U \right) d^{3(N-1)} R' / [C_0 \Gamma(3(N-1)/2 + 1)]. \end{aligned} \quad (21)$$

Taking the volume derivative of the entropy using this form for the phase volume leads to

$$P = 3(N-1)k_B T/2 - \langle \partial U / \partial V \rangle, \quad (22)$$

where the first term is called the ideal gas contribution and the second term the internal force contribution. The evaluation of the volume derivative of U was discussed in detail by Ray [14]. This is the correct expression for the pressure that can be directly found from Newton's laws and the virial theorem. In both the *EVN* and *EVNM* ensembles the expression for the pressure has an N instead of $N-1$ in the ideal gas contribution because the boost constraint is not included in those ensembles [4,5,7]. This finally is the correction to the pressure in Refs. [4,5] and shows that the correct ensemble to use in molecular dynamics is the *EVNMG* ensemble. In general, relations involving the momenta, such as, for example, Eq. (19), will be the same in the *EVNM* and *EVNMG* ensembles but volume derivatives of the entropy and related quantities will differ by factors of $N-1$ replacing N . This would change the general volume derivative expressions given by Lustig [8] for the correct molecular dynamics ensemble.

Occasionally one sees simulations in which, to take the reduction of spatial degrees of freedom by 3 into account, it is assumed that one of the particles, say particle 1, is held at a fixed position. The effect of this is to introduce a delta function $\delta(\mathbf{a} - \mathbf{r}_1)$, with \mathbf{a} the fixed position, into the phase volume instead of the boost δ function in Eq. (10). There would also be the constraint that the momentum of particle 1 be zero $\delta(\mathbf{p}_1)$. These two δ functions would replace the total momentum constraint and boost constraint in the phase volume in Eq. (10) and would yield a different ensemble. It is clear that this would lead to the same $N-1$ as in Eqs. (19) and (22). The total momentum would not be constant because it requires an external force to hold particle 1 at a fixed position, however, the energy would be constant because this

external force does no work. Thus, this ensemble may be used in molecular dynamics simulations and has some advantages because one does not need to introduce Jacobi coordinates and momenta. However, it is somewhat arbitrary and artificial because it does not really correspond to conditions associated with a real physical system.

IV. CONCLUSIONS

We have demonstrated that the correct molecular dynamics ensemble is the *EVNMG* ensemble or in Nosé canonical ensemble molecular dynamics the *TVNMG* ensemble, with $\mathbf{M}=0$. The only assumptions are that Newton's laws describe the system's motion and periodic boundary conditions are employed. The differences between results in the *EVN*, *EVNM*, and *EVNMG* ensembles are of order $(1/N)$ and are small for large N , however, it is important to recognize the correct ensemble corresponding to molecular dynamics simulations and for small systems the differences could be important. The constants of the motion \mathbf{G} have appeared in statistical mechanics before, for example, in association with Monte Carlo studies of isolated clusters [15].

Fluctuation formulas for thermodynamics response functions, such as specific heat, elastic constants, thermal expansion coefficient, etc. can be derived for the molecular dynamics ensemble just as in any shell ensemble [4,5,7,8,16]. Equation (17) gives the ensemble average in the molecular dynamics ensemble. The time average over trajectories in a molecular dynamics calculation correspond to this theoretical average. Note also that this average can be calculated using the Metropolis Monte Carlo method with the importance function given by Eq. (16) just as in any shell ensemble [17–19]. Although the *EVN* ensemble is almost universally associated with molecular dynamics, it is ironic that molecular dynamics, as it is usually implemented, does not generate this ensemble but the molecular dynamics ensemble *EVNMG*. The Metropolis Monte Carlo method can be used to generate the *EVN*, *EVNM*, and *EVNMG* ensembles but only the latter can be generated using molecular dynamics. It is clear that even in an inertial frame for which $\mathbf{M}=0$, $\mathbf{G}=0$, there is a difference between the *EVN*, *EVNM*, and *EVNMG* ensembles because of the $N-1$ factors. The boost constraint would also influence other extended variable molecular dynamics methods which are used to numerically generate other ensembles, such as Andersen's [20] isoenthalpic-isobaric ensemble, the isothermal-isobaric ensemble, as well as the tensor versions of these ensembles discussed by Parrinello and Rahman [21] and Ray and Rahman [22].

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